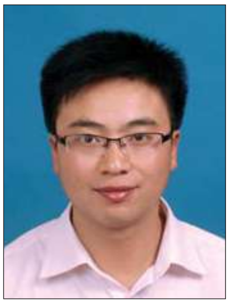

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MECHANICAL AND TRIBOLOGICAL PERFORMANCE OF TC4 ALLOY WITH SURFACE PLASMA MOLYBDENIZATION

DOI 10.15589/SMI. 20170106

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Abstract. A plasma molybdenized layer has been applied on titanium alloy TC4 by double-glow plasma surface alloying technique (DPSA) to improve its wear resistance. The distribution of the microstructures, morphology and composition of the molybdenized layer are analyzed by means of scanning electronic microscopy (SEM) and X-ray diffraction (XRD). The alloying layer is composed of the Mo-deposited layer 12 μm thick and the Mo-diffused layer 15 μm thick. Mo exists in the form of pure element and its solid solution (Ti, Al8, Mo, V). The mechanical properties of the molybdenized layer are evaluated by means of a nano-indentation test. The nano-hardness and elasticity modulus of the surface-modified layer are 13.832 GPa and 804.27 GPa, respectively. These values are much higher than those of the TC4 substrate. The tribological behavior is studies by means of dry sliding in the ball-on-disc mode under different loads (1.3–11.3N) and sliding speeds (5, 10, 15, 20 m/min). The friction coefficient and specific wear ratio of the molybdenized layer decrease greatly if compared to those of the TC4 bare metal.

Keywords: double-glow plasma surface alloying; tc4 alloy; plasma molybdenization; tribological performance.

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Problem statement. Titanium and its alloys, such as TC4, are widely applied in aerospace, ship navigation, mechanical engineering, chemical and bioengineering due to their high strength/weight ratio, high-temperature strength, excellent corrosion resistance and biocompatibility. However, titanium alloys suffer from the serious disadvantage of poor wear resistance, which prevents them from being more widely applied [1–3]. Numerous surface engineering technologies have been developed to enhance the wear resistance of titanium alloys while maintaining their corrosion resistance and biocompatibility, such as plasma nitriding [4], carburizing [5], PVD [6–7] and ion implantation [8–9]. However, there are still some unsatisfactory results for the use of those processes. For example, nitriding or carburizing may result in a brittleness induced by the diffusing of hydrogen. The hardening thicknesses of a PVD coating or an ion implantation layer are too small to support a heavy loading. As an attempt to solve the problems mentioned above, the molybdenized layer was carried out on the TC4 substrate using a novel surface engineering process, double-glow plasma surface alloying (DPSA) [10–12].

THE ARTICLE AIM is to characterize the compositions, microstructures, mechanical and tribological properties of the molybdenized layer obtained by this technology.

Basic material

1. Experimental procedure

1.1. Materials and preparation of modified layer

TC4 alloy samples (15mm × 15mm × 4mm) were obtained from an annealed TC4 board by cutting. The chemical composition of the alloy is given in Table 1. Before molybdenizing, the sample substrate was polished using the metallographic method to ensure the surface roughness R_a < 0.1μm. A molybdenum plate (purity: 99.95 %, Φ100 mm × 3.5 mm) was used as the supply source of the alloying element. The working gas was Ar.

The molybdenized layer was applied in a double-glow plasma surface alloying furnace, where a low-temperature plasma has been produced by a glow discharge process in a vacuum sputtering chamber [13]. The schematic diagram of the working principle is shown in Fig. 1.

There were three electrodes in the chamber: an anode, a negative cathode (sample) and a sputtering source cathode (pure Mo target). Two glow discharges were ignited on the target and substrate separately with two different voltages supplied to heat them to a high temperature. As the bombard of argon ions took place, Mo particles were sputtered away from the target and deposited on the TC4 substrate surface. The alloying layer was formed thereafter through a thermal diffusion process. The thickness and surface composition of the alloying layer could be controlled by varying the processing parameters.

The parameters of this experiment were selected as follows: the source electrode voltage of 900 V, the workpiece voltage controlled at 400 V, the distance from the sample to the source target of 15 mm, the working pressure of 35 Pa, the temperature of 900 °C, and the duration of diffusion of 3 hours.

1.2. Microstructures and chemical compositions

The molybdenized layer was examined by X-ray diffraction (BurkerD8-ADVANCE) for phase identification using the Cu Ka radiation. The cross-section morphology of the molybdenized layer was observed by scanning electron microscopy (SEM, JEOL JSM-6360). The chemical composition of the molybdenized layer was examined by energy dispersive spectroscopy (EDS, LINK-860).

1.3. Nano-indentation and micro-hardness test

The mechanical properties of the molybdenized layer were studied using a nano-indentation test. A diamond indenter pyramid shaped with an angle of 115° between opposite faces was employed in the experiment. The other parameters were: test force of 100 mN, load speed of 1.32 mN/sec, and holding time of 10 sec.

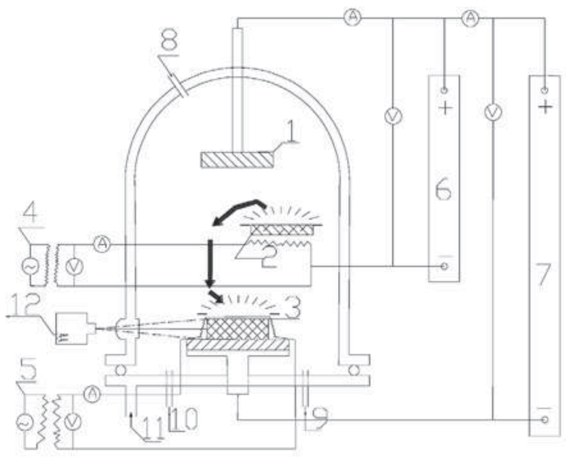

Fig. 1. Schematic illustration of the DPSA:
1 — anode; *2* — source cathode (target); *3* — negative cathode (sample); *4* — source heating power supply; *5* — cathode heating power supply; *6* — source power supply; *7* — cathode power supply; *8* — import of inert gas; *9* — exit of inert gas; *10* — interface of vacuum equipment; *11* — cooling water; *12* — pyrometer

Table 1. Chemical composition of TC4 board (wt. %).

Al	V	Si	Fe	C	O	N	H	Ti
6.60	4.21	0.07	0.30	0.03	0.14	0.015	0.003	Bal.

1.4. Wear test

The tribological behavior of the molybdenized layer and TC4 substrate was investigated under different loads (1.3 – 11.3 N, the load was increased by 1 N every time) and sliding speeds (5, 10, 15, 20 m/min) by means of a dry sliding test in the ball-on-disc mode at room temperature. A GCr15 ball (nominal hardness of 62 HRC) with the diameter of 4.75 mm was used as a counter-body. The test parameters are shown in Table 2. The weight loss of the specimens was estimated by the analytical balance with accuracy of 0.1 mg, before and after the wear test.

The wear volume was calculated based on the three-dimensional surface profilometry measured with a Micro-XAM Surface Mapping Microscope (SMM). Further, the specific wear ratio was calculated by dividing the wear volume by the load and sliding distance. Post-wear examination of the worn track was conducted using SEM, EDS and SMM.

2. Results and Discussion

2.1 Microstructures and compositions

Fig. 2 shows the surface of the molybdenized layer applied onto the TC4 substrate. The results show that the molybdenized layer is silver white and composed of the pyramid-like particles. Its surface is uniform, without holes, cracks and impurities. Obviously, the pyramid-like particles are the top of the columnar grain clusters. This kind of surface morphology may be caused by the reasons given below.

1. As the amount of molybdenum atoms deposited on the surface increases, Mo grains are formed and growing continuously. The increase id developed in the mechanism of island-like growing due to prior direction, and finally columnar grains are formed.

2. During the deposition, the as-deposited atoms, clusters and particles suffered from the bombardment of hybrid plasma. Some small atom clusters and particles were sputtered out, which made the outer surface rough.

Typical cross-section micrograph and concentration profiles of the molybdenized layer are showed in Fig. 3 and Fig. 4. The distribution of alloying elements along the depth was detected by linear scanning analysis from point A to point B in Fig. 3. The molybdenized layer is composed of the Mo-deposited layer and the Mo-defused layer. Since molybdenum possesses infinite solubility in titanium, the diffusing layer was basically a solid solution of molybdenum in the matrix with a gradient concentration profile, and no distinctive interface was observed between the deposited layer and the bulk of the substrate. As shown in Fig. 3, zone I is the Mo-deposited layer in which the main alloying element is pure molybdenum. Zone II beneath the depositing layer is an inter-diffusion layer where Ti, Al, V in the substrate were diffused into the coating and molybdenum was diffused into the substrate. This inter-diffusion between the Mo-deposited layer and the substrate formed a transition zone that is beneficial to the interfacial bonding strength of the modified layer. The deposited layer and the inter-diffusion layer are defined as the molybdenized layer in this paper, and its thickness is about 30 μm. Zone III beneath the inter-diffusion layer is the TC4 substrate where molybdenum almost could not be detected. The combination of the three zones has a very high quality, does not feature voids, holes and impurities.

Fig. 5 and Fig. 6 show the XRD pattern of the molybdenized layer. Fig. 5 shows that the XRD pattern for the Mo-deposited layer can be assigned to the dominating molybdenum phases with (211) orientation. Fig. 6 shows the XRD pattern for the Mo inter-diffusion layer. For the alloyed layer, the intermetallic compound AlTi2 and (Ti, Al8, Mo, V) were identified. The XRD data revealed that the molybdenized layer deposited on the TC4 substrate is a mixture of crystalline phases. The EDS pattern reflects a result corresponding to that of the XRD analysis.

Table 2. Conditions of wear test

Factor		Load, N	Time/min
Sliding speed (m/min)	5	1.3~11.3	60
	10		
	15		
	20		

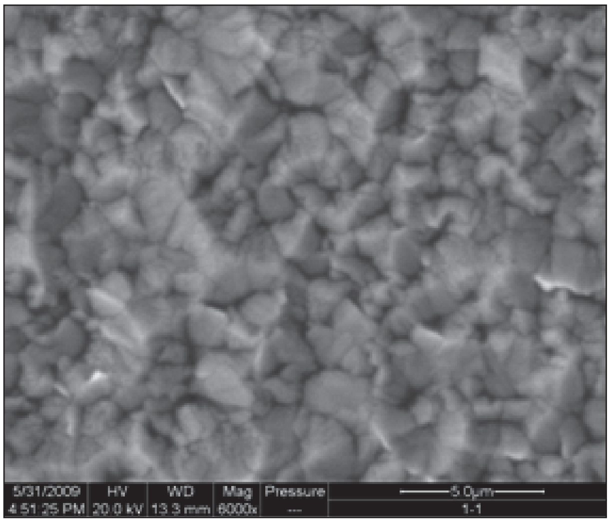

Fig. 2. SEM images of the molybdenized layer surface

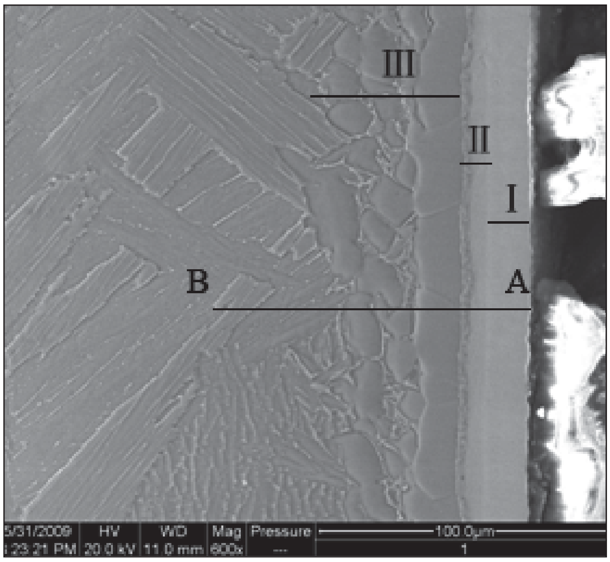

Fig. 3. Cross-section micrograph of the molybdenized layer

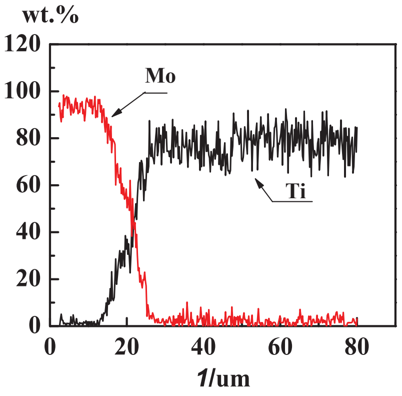

Fig. 4. EDS element distribution curves of the molybdenized layer

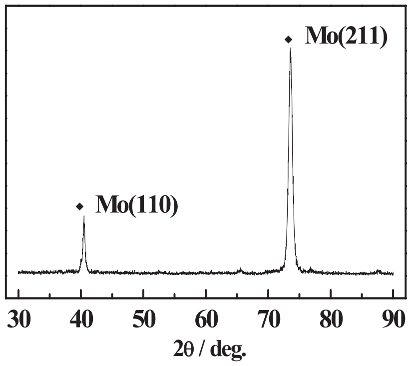

Fig. 5. X-ray diffraction patterns of the Mo-deposited layer

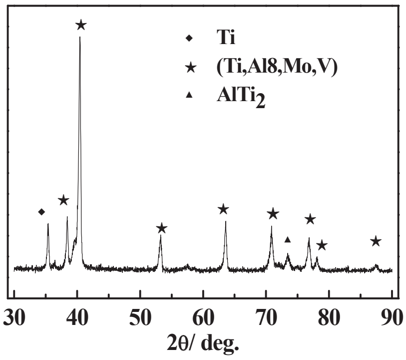

Fig. 6. X-ray diffraction patterns of the Mo inter-diffusion layer

2.2 Mechanical properties

Fig. 7 shows the indentation force-depth curve of the molybdenized layer and the TC4 substrate. As can be seen from the graph, the P-h curve of the Mo-modified layer is continuously changed throughout the loading and unloading process, without any steps. This evidences a high toughness of the molybdenized layer and the absence of fracture. The nano-indentation test detailed results are shown in Table 3. The mechanical behavior of the molybdenized layer can be reflected by two parameters, hardness and elasticity modulus [14]. The value of nano-hardness for the molybdenized layer is 13.832 GPa, which is about four times that of the TC4 substrate, and the elasticity modulus also had a considerable enhancement. There are two reasons for the improvement. On the one hand, the Mo-deposited layer improves the surface hardness of the TC4. On the other hand, Mo and Ti form the substitutional solid solution of titanium lattice, c lattice increases in axial length, with the axial length a increase of less than c/a, resulting in the shaft increase, and the lattice distortion hindering the dislocation motion. The Mo inter-diffusion layer has a good transition to the hardness of the surface deposition layer and the matrix, and has a good supporting effect on the highly hard surface layer.

2.3 Tribological properties

2.3.1. Wear resistance performance

The tribological behavior of the molybdenized layer and TC4 substrate was investigated under different loads (1.3 – 11.3N, the load increased by 1 N every time) and sliding speeds (5, 10, 15, 20 m/min) by means of a dry sliding test in the ball-on-disc mode at room temperature. Fig. 8 is the wear map of the molybdenized layer and TC4 substrate, which shows the relationship of the wear rate between the load and sliding speed. As Fig. 8 reveals, the specific wear rate of TC4 is much higher than that of the molybdenized layer. At that, there is a general tendency of the specific wear rate increasing with the rise of the load. As shown in Fig.8 *a*, *c*, *e*, *g*, when the sliding speed is low (5, 10 m/min), the specific wear rate of TC4 is higher than that under higher sliding speed (15, 20 m/min).

In order to study the wear mechanism of the molybdenized layer in detail, the sample with the sliding speed of 20 m/min and the load of 3.3 N is chosen for analysis in this paper. Table 4 shows the wear results of the molybdenized layer and the TC4 substrate. It can be seen that the specific wear rate of the modified layer is much lower than that of the substrate under the same conditions. The specific wear rate of the molybdenized layer is $0.232 \cdot 10^{-5}$ $mm^3 \cdot N^{-1} \cdot m^{-1}$, about 1/160 of that of the TC4 substrate under the same conditions, reflecting the excellent wear resistance and achieving the purpose of improving the wear resistance of titanium alloy.

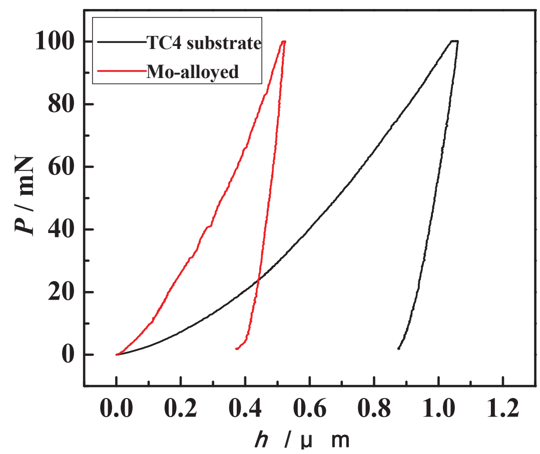

Fig. 7. Loading-unloading curve for the molybdenized layer and the substrate

Table 3. Mechanical properties of the molybdenized layer and the TC4 substrate

Sample	Maximum depth *h*max / µm	Residual depth *hr*, µm	Maximum dynamic hardness *DHT*115	Martens hardness *HM*115, GPa	Modulus of elasticity *E*, GPa
Mo-alloyed	0.523	0.378	1410.486	13.832	804.27
TC4 substrate	1.059	0.876	344.423	3.373	159.17

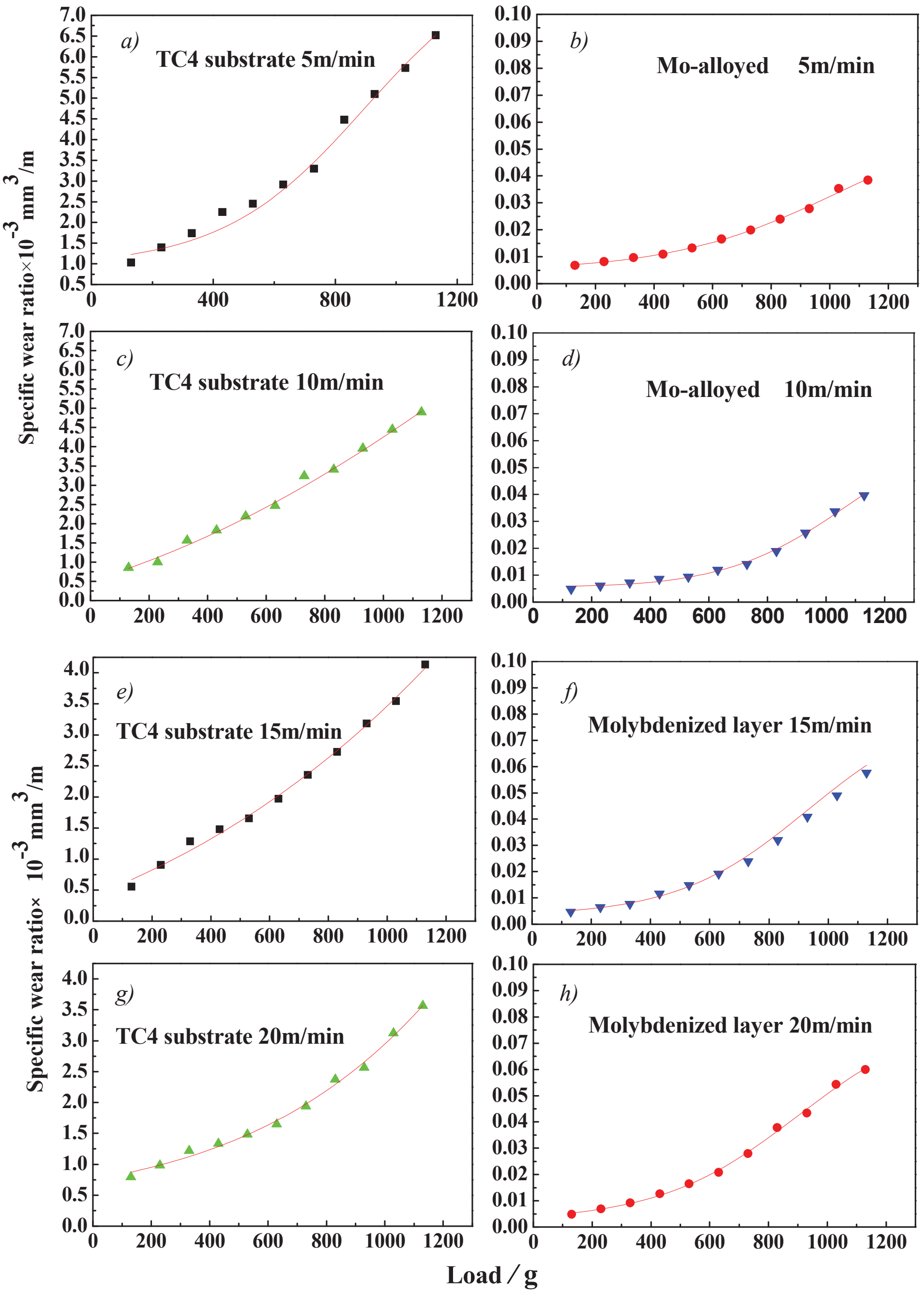

Fig. 8. Wear maps under different sliding speed

Table 4. Wear results of the molybdenized layer and the TC4 substrate

Sample		Scar width b, mm	Scar depth h, µm	Wear volume V_w, mm^3	Wear rate v, mm^3·m^{-1}	Specific wear ratio K, mm^3·N^{-1}·m^{-1}	Wear loss m, mg
20m/min 3.3N	TC4 substrate	1.675	69.5	$14.64 \cdot 10^{-1}$	12.2·10-4	$36.97 \cdot 10^{-5}$	8.5
	Mo-alloyed	0.563	1.3	$0.092 \cdot 10^{-1}$	$0.077 \cdot 10^{-4}$	$0.232 \cdot 10^{-5}$	0.2

2.3.2 Friction coefficient profiles

Fig. 9 shows the friction coefficients of the molybdenized layer and the TC4 substrate sliding against GCr15 ball at room temperature without lubrication. The results show that the value of the friction coefficient of the molybdenized layer was lower and more stable than that of TC4 substrate. The frictional behavior of the molybdenized layer is strongly affected by its mechanical properties [15]. It is known that the friction coefficient decreases as the hardness increases [16]. The average value of the friction coefficient of the molybdenized layer is approximately 0.5. To the opposite, the average value of the friction coefficient of the TC4 substrate is 0.65, exhibiting an unsteady characteristic. This result may be attributed to the adhering-shearing displaced repeatedly during the whole experiment.

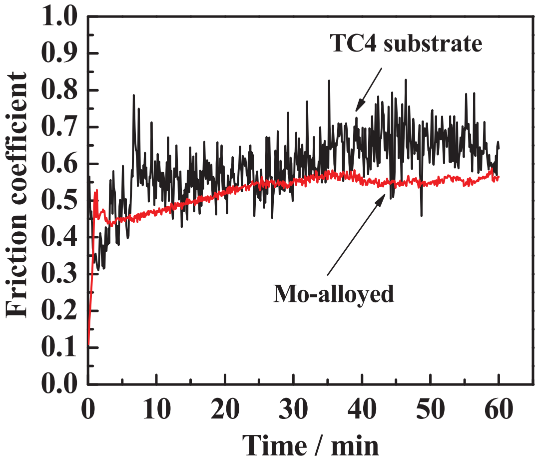

Fig. 9. Friction coefficient profiles (20m/min and 3.3N)

2.3.3 Wear mechanism

Fig. 10 shows that both depth and width of the wear tracks in the molybdenized layer are much smaller than those in TC4 samples in the initial state. The wear depth observed in the TC4 sample in initial state is 69.5 µm, while the that for the molybdenized layer is just 1.3 µm. On the other hand, the wear widths of bare TC4 and the molybdenized layer are 1.675 mm and 0.563 mm, respectively (Fig.10, *a*, *c*). Continuous sliding marked the worn surface of TC4with cross-plastic deformation, ploughing, smearing and severe plastic deformation (Fig. 10, *b*), whereas the surface of the molybdenized sample is relatively smooth and has no grooves after tests (Fig.10, *d*).

The wear resistance of titanium alloy after plasma surface molybdenization has been greatly improved, which is attributed to the high hardness of the molybdenized layer. To reveal the wear mechanism, EDS analyses on the wear tracks were carried out. As shown in Fig. 11, there are mainly Mo elements and O elements, almost no Ti elements, which can guarantee that the Mo-modified layer does not rupture and shows the TC4 substrate after wearing. It shows that the molybdenized layer has a high wear resistance and peeling resistance.

Compared with Fig. 11 a-b, the oxygen content of the molybdenized layer is higher, about 55.66%. Under the same conditions, the atomic percentage of oxygen in the wear track of the TC4 is 10.98%, only 1/5 of the oxygen content in the modified Mo layer. The large difference in the content of oxygen is a great help in explaining the difference in wear resistance between the molybdenized layer and TC4 substrate. It can be inferred that there is a thin oxide film on the surface of the Mo-modified layer during the ball-on-disc wear test, which can slow down the wear to a certain extent. The dominant wear mechanism of the molybdenized layer is oxidative wear and abrasive wear. Whereas, because the thin oxide film is difficult to form, wearing of the bare TC4 is dominated by adhesion wear and plough wear.

CONCLUSIONS. In order to improve the tribological properties of TC4 alloy, the molybdenized layer has been applied onto the TC4 samples surface by means of double-glow plasma alloying. The following conclusions are drawn from the study:

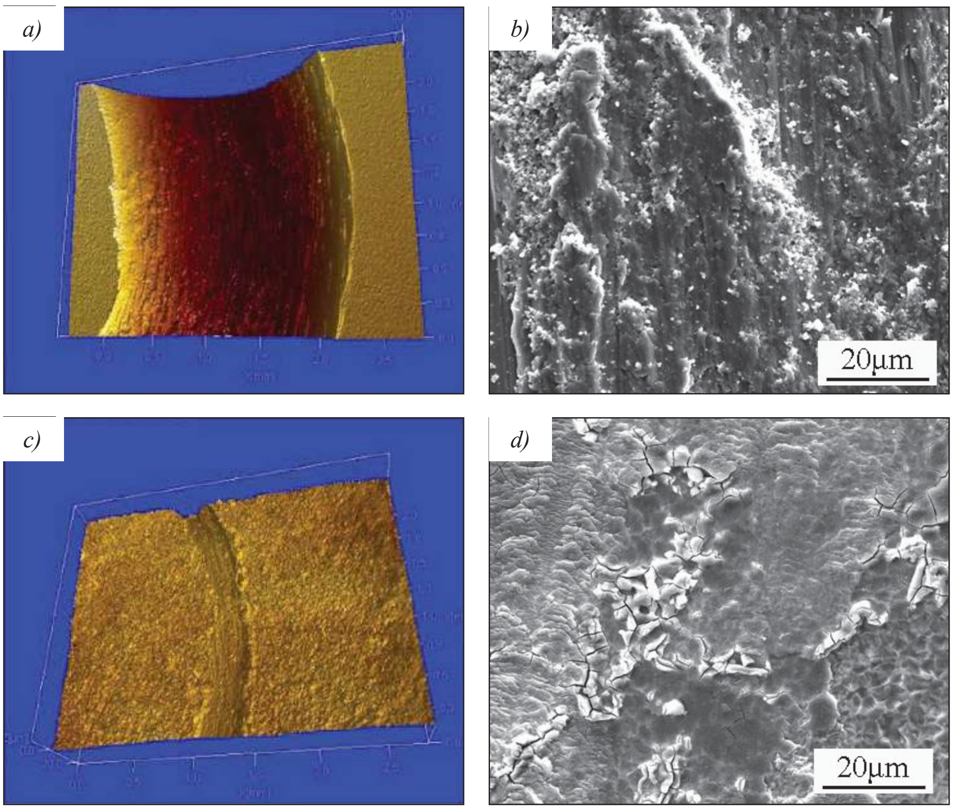

Fig. 10. 3D-surface profilometries and SEM morphologies of the wear tracks after rubbing at 20m/min:
a, *b* — substrate; *c*, *d* — Mo-alloyed layer

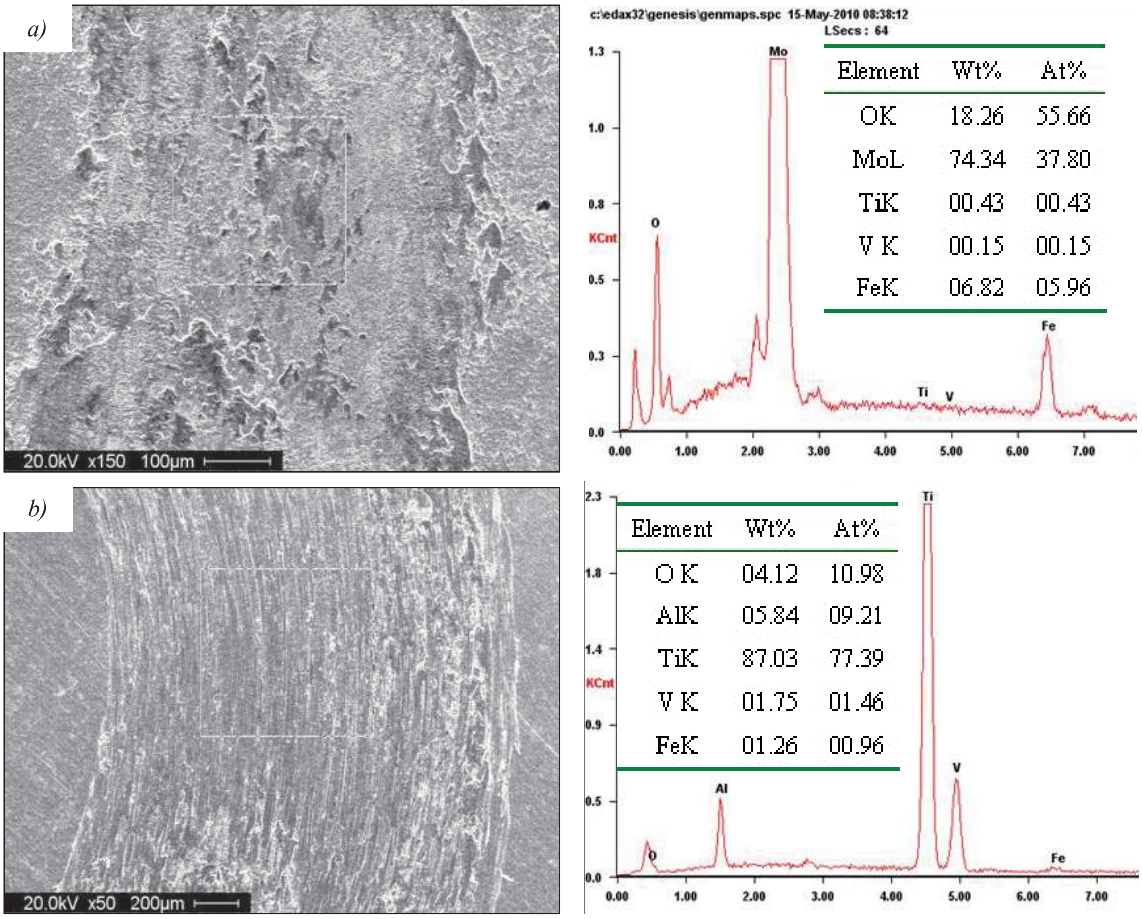

Fig. 11. EDS profiles of the wear tracks:
a — Mo-alloyed layer; *b* — substrate.

1. The molybdenized layer is composed of the Mo-deposited layer 12 μm thick and the Mo-defused layer 15 μm thick from surface to matrix. The molybdenum distribution of the molybdenized layer is a gradient distribution on the cross-section. According to the XRD analysis, the main phase structures of the molybdenized layer are Mo and (Ti, Al8, Mo, V) phases.

2. The nano-hardness and elasticity modulus of the molybdenized layer are 13.832 GPa and 804.27 GPa, which are much higher than those of the TC4 substrate.

3. The wear test has indicated that the friction coefficient and specific wear ratio of the molybdenized layer are smaller than that of the TC4 substrate, which is attributed to its high hardness. The dominant wear mechanisms of the molybdenized layer are oxidative wear and abrasive wear, whereas the wearing of the bare TC4 is dominated by adhesion wear and plough wear.

Статью рекомендует в печать
д-р техн. наук, проф. *А. Н. Дубовой*

FOUNDATION PROJECT:

A Project Supported by Scientific Research Fund
of Yancheng Institute of Industry Technology (No.:ygy1405).